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Late Pliocene marine $p\text{CO}_2$ reconstructions from the Subarctic Pacific Ocean

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Key Points:

- Subarctic Pacific Ocean carbon dynamics reconstructed using diatom carbon isotopes
- Net ocean-atmosphere CO_2 flux does not alter over the onset of major Northern Hemisphere Glaciation (c. 2.75-2.73 Ma).

13 Abstract

14 The development of large ice-sheets across the Northern Hemisphere during the late Pliocene
 15 and the emergence of the glacial-interglacial cycles that punctuate the Quaternary mark a
 16 significant threshold in Earth's climate history. Although a number of different mechanisms have
 17 been proposed to initiate this cooling and the onset of major Northern Hemisphere glaciation,
 18 reductions in atmospheric concentrations of CO₂ likely played a key role. The emergence of a
 19 stratified (halocline) water column in the subarctic north-west Pacific Ocean at 2.73 Ma has
 20 often been interpreted as an event which would have limited oceanic ventilation of CO₂ to the
 21 atmosphere, thereby helping to cool the global climate system. Here, diatom carbon isotopes
 22 ($\delta^{13}\text{C}_{\text{diatom}}$) are used to reconstruct changes in regional carbon dynamics through this interval.
 23 Results show that the development of a salinity stratification did not fundamental alter the net
 24 oceanic/atmospheric flux of CO₂ in the subarctic north-west Pacific Ocean through the late
 25 Pliocene/early Quaternary. These results provide further insights into the long-term controls on
 26 global carbon cycling and the role of the subarctic Pacific Ocean in instigating global climatic
 27 changes.

28 1 Introduction

29 Understanding the processes associated with the progressive Late Pliocene glaciation of
 30 the Northern Hemisphere remains an essential objective for understanding the long-term
 31 functionality and temporal variability of the global climate system (Mudelsee and Raymo, 2005).
 32 Of particular note is the transition associated with the onset of major Northern Hemisphere
 33 Glaciation (oNHG) and its intensification (iNHG) from c. 2.75-2.73 Ma onwards in MIS G6
 34 when significant ice-sheets developed across Greenland, Eurasia and Northern America (Raymo
 35 et al., 1994; Maslin et al., 1996; Kleiven et al., 2002; Matthiessen et al., 2009; Bailey et al.,
 36 2013). Instrumental to this transition are Late Pliocene changes in solar insolation, tectonic
 37 uplift, water column stratification and the opening/closure of oceanic gateways, all of which
 38 triggered oceanic/atmospheric feedbacks that initiated cooler conditions and the increased supply
 39 of moisture to high-latitude continental regions (Ruddiman and Kutzbach, 1989; Driscoll and
 40 Haug, 1998; Haug and Tiedemann, 1998; Maslin et al., 1998; Ravelo et al., 2004; Sarnthein et
 41 al., 2009; Brierley and Fedorov, 2016).

42 The extent to which variations in atmospheric $p\text{CO}_2$ ($p\text{CO}_{2(\text{atm})}$) played a role in triggering
 43 both the oNHG and iNHG remains unconstrained. Ocean-atmospheric models have
 44 demonstrated that reductions in $p\text{CO}_{2(\text{atm})}$ were probably critical in both instigating and sustaining
 45 the development of large ice-sheets through the oNHG (Lunt et al., 2008, 2010; Bonelli et al.,
 46 2009; Frank et al., 2010; Willeit et al., 2015), a view supported by most but not all $p\text{CO}_{2(\text{atm})}$
 47 reconstructions (e.g., Pagani et al., 2010; Seki et al., 2010; van de Wal et al., 2011; Badger et al.,
 48 2013; Martínez-Botí et al. 2015; Willeit et al., 2015; Stap et al., 2016). With any significant
 49 change in $p\text{CO}_{2(\text{atm})}$ likely linked to oceanic-atmosphere exchanges, a need exists to identify and
 50 evaluate possible marine sources/sinks of CO₂ through the late Pliocene.

51 1.1 Subarctic north-west Pacific Ocean

52 The subarctic north-west Pacific Ocean (Fig. 1) is one location that may have
 53 experienced significant changes in ocean-atmospheric carbon dynamics through the late Pliocene
 54 and iNHG. Today the subarctic north-west Pacific Ocean acts as a net sink of atmospheric CO₂
 55 due to a halocline driven stratification at a depth of c. 150-200 m that minimizes deep water

exposure at the ocean-atmosphere interface (Tabata, 1975; Honda et al., 2002; Chierici et al., 2006) (Fig. 1). Proxy-data records from ODP Site 882 indicate that the halocline developed over the iNHG at 2.73 Ma with increases in surface freshwater transforming the mixed water column to a stratified system (Sigman et al., 2004; Haug et al., 2005; Swann et al., 2006; Swann, 2010). This development altered regional biogeochemical cycling (Reynolds et al., 2008; Shimada et al., 2009; Bailey et al., 2011; Studer et al., 2012; Swann et al., 2016) with a drop in opal mass accumulation rates (MAR) from c. 3 g cm⁻² ka⁻¹ to <1 g cm⁻² ka⁻¹ at 2.73 Ma (Haug et al., 1999; Sigman et al., 2004).

These changes observed in the subarctic North Pacific Ocean may also have dramatically impacted ocean-atmosphere exchanges of CO₂. With the deep North Pacific Ocean enriched in CO₂ relative to other ocean basins with dissolved inorganic carbon at >2,300 μmol kg⁻¹ (Lauvset et al. 2016), a mixed water column prior to 2.73 Ma characterized by deep water upwelling may have ventilated CO₂ to the atmosphere, thereby helping to maintain the warm Pliocene climatic state (Haug et al., 1999). The emergence of a halocline from 2.73 Ma would have then minimized such exchanges, transforming the region to a net sink of atmospheric CO₂ similar to the modern day. This alteration in the direction of net ocean-atmosphere CO₂ exchange would have aided the iNHG and the global shift to colder climatic conditions (Haug et al., 1999). In an attempt to constrain the role of the subarctic Pacific in regulating the global climate system and *p*CO_{2(atm)} in the Piacenzian (3.60-2.58 Ma), diatom carbon isotopes (δ¹³C_{diatom}) are employed to reconstruct carbon dynamics in the subarctic north-west Pacific Ocean and assess their response to the expansion of ice sheets across the Northern Hemisphere over the iNHG and the transition to a stratified water column.

1.2 Reconstructing *p*CO₂ from δ¹³C_{diatom}

Hitherto, estimates of marine *p*CO₂ (*p*CO_{2(aq)}) and *p*CO_{2(atm)} have been derived from the boron isotopes (δ¹¹B) of foraminifera (Foster and Rae, 2016), the δ¹³C composition of alkenones (Pagani, 2002), B/Ca measurements in foraminifera (Yu et al., 2007), fossil leaf stomata (Bai et al., 2015) and pedogenic carbonate (Montañez et al., 2016). Although each approach contains uncertainties and assumptions, the combination of approaches together with model simulations (van de Wal et al. 2011; Stap et al. 2016) are providing increasing consensus on the magnitude of past *p*CO_{2(atm)} and on the drivers, responses and climate sensitivity of the earth system.

Emerging work has promoted the use of δ¹³C_{diatom} to reconstruct *p*CO_{2(atm)} (Heureux and Rickaby, 2015; Mejía et al., 2017; Stoll et al., 2017). The intrinsic organic carbon matter in diatoms frustules is comprised of proteins and polyamines that forms a key template for diatom biomineralisation (Hecky et al., 1973; Swift and Wheeler, 1992; Kröger et al., 1999, 2000; Sumper and Kröger, 2004). During the photosynthetic production of this organic matter, diatoms preferentially fractionate ¹²C over ¹³C with the isotopic composition of δ¹³C_{diatom}:

$$\delta^{13}\text{C}_{\text{diatom}} = \delta^{13}\text{C}_{\text{DIC}} - \varepsilon_p - (\varepsilon_f - \varepsilon_p) \frac{C_i}{C_e}$$

(Eq. 1)

where δ¹³C_{DIC} is the isotopic value of the Dissolved Inorganic Carbon (DIC) substrate; ε_p is the isotopic fractionation for the diffusion of carbon into the cell; ε_f is the isotopic fractionation associated with carbon capture by the photosynthetic enzyme RuBisCO having been constrained at +25‰ by Bidigare et al. (1997) and where C_i and C_e are the intra- and extra-cellular concentrations of CO₂ in the water column (CO_{2(aq)}) (Laws et al., 1995; Rau et al., 1996, 1997).

Accordingly, $\delta^{13}\text{C}_{\text{diatom}}$ can be linked to factors including changes in: 1) $\delta^{13}\text{C}_{\text{DIC}}$ arising from changes in ocean circulation and the production/dissolution of carbonate producers; 2) photic zone $p\text{CO}_{2(\text{aq})}$ with increases (decreases) triggering a corresponding decrease (increase) in $\delta^{13}\text{C}_{\text{diatom}}$ through modification of $\text{C}_i:\text{C}_e$; and 3) photosynthetic carbon demand with increases causing a ^{12}C depletion in ambient seawater and so increasing $\delta^{13}\text{C}_{\text{diatom}}$. Attempts to reconstruct $p\text{CO}_{2(\text{aq})}$ have mainly focused on ε_p (the fractionation between diatom bound carbon and $\text{CO}_{2(\text{aq})}$):

$$\varepsilon_p = \left[\frac{\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}} + 1000}{\delta^{13}\text{C}_{\text{diatom}} + 1000} - 1 \right] \cdot 10^3$$

(Eq. 2)

In turn, $\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}}$ can be calculated from the $\delta^{13}\text{C}$ of planktonic carbonate ($\delta^{13}\text{C}_{\text{carbonate}}$), such as a planktonic foraminifera, building on the temperature-dependent fractionation between HCO_3^- and $\text{CO}_{2(\text{aq})}$ at a given sea surface temperature (T) (Mook et al., 1974; Romanek et al., 1992):

$$\delta^{13}\text{C}_{\text{CO}_{2(\text{aq})}} = \left(\frac{\varepsilon_{\text{CO}_{2(\text{aq})}-\text{CO}_{2(\text{g})}} + 1}{1000} \right) \cdot (\delta^{13}\text{C}_{\text{CO}_{2(\text{g})}} + 1000) - 1000$$

(Eq. 3)

$$\varepsilon_{\text{CO}_{2(\text{aq})}-\text{CO}_{2(\text{g})}} = \frac{-373}{T + 273.15} + 0.19$$

(Eq. 4)

$$\delta^{13}\text{C}_{\text{CO}_{2(\text{g})}} = \frac{\delta^{13}\text{C}_{\text{carbonate}} + 1000}{\varepsilon_{\text{calcite}-\text{CO}_{2(\text{aq})}} / 1000 + 1}$$

(Eq. 5)

$$\varepsilon_{\text{calcite}-\text{CO}_{2(\text{g})}} = 11.98 - 0.12T$$

(Eq. 6)

By targeting marine sediments in which both diatoms and planktonic foraminifera are preserved in the sediment record, $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{13}\text{C}_{\text{foram}}$ can be combined to obtain absolute values of $\text{CO}_{2(\text{aq})}$ in the ambient photic zone waters:

$$\text{CO}_{2(\text{aq})} = \frac{b}{\varepsilon_f - \varepsilon_p}$$

(Eq. 7)

where ε_f is the isotopic fractionation during carbon fixation which has been constrained as 25‰ (Bidigare et al., 1997) and b is the combination of physiological factors relating to cell size and growth rate. From this relationship, $p\text{CO}_{2(\text{aq})}$ can be calculated using Henry's law via the solubility coefficient K_H (Weiss 1970, 1974):

$$p\text{CO}_{2(\text{aq})} = \frac{\text{CO}_{2(\text{aq})}}{K_H}$$

(Eq. 8)

from which differences between $p\text{CO}_{2(\text{aq})}$ and $p\text{CO}_{2(\text{atm})}$ can be calculated as:

$$\Delta p\text{CO}_2 = p\text{CO}_{2(\text{aq})} - p\text{CO}_{2(\text{atm})}$$

139

(Eq. 9)

140 In instances where equilibrium exists between the surface ocean and the atmosphere,
 141 $\Delta p\text{CO}_2$ should be zero. Where the two system are not in equilibrium $\Delta p\text{CO}_2$ provides insights
 142 into the net exchange between the two systems with positive (negative) values of $\Delta p\text{CO}_2$
 143 indicating the marine system acts a source (sink) of atmospheric CO_2 .

144 An advantage in using $\delta^{13}\text{C}_{\text{diatom}}$ to reconstruct $p\text{CO}_{2(\text{aq})}$ is the widespread abundance of
 145 well preserved diatoms in sediments across the globe, particularly in polar regions where
 146 carbonates are not readily preserved. However, whilst clear evidence exists that diatom carbon
 147 fixation is linked to $\text{CO}_{2(\text{aq})}$ (Popp et al. 1998; Rosenthal et al., 2000), reconstructions of $p\text{CO}_{2(\text{aq})}$
 148 require robust estimates of b that accounts for physiological fractionation effects in $\delta^{13}\text{C}_{\text{diatom}}$
 149 including those related to growth rate and cell size (Bidigare et al., 1997; Laws et al., 1995,
 150 2002). For example, alkenone $\delta^{13}\text{C}$ reconstructions of $p\text{CO}_{2(\text{aq})}$ rely on the strong relationship
 151 between b and PO_4^{3-} concentrations in the modern water column (Bidigare et al 1997; Pagani et
 152 al., 2005). Recent work has demonstrated a strong link between b in diatoms and measures of
 153 productivity/growth rate such as opal concentrations, thereby allowing reconstructions of
 154 $p\text{CO}_{2(\text{aq})}$ from $\delta^{13}\text{C}_{\text{diatom}}$ (Heureux and Rickaby, 2015; Stoll et al., 2017).

155 2 Methods

156 ODP Site 882 lies at the western section of the Detroit Seamounts (50°22'N, 167°36'E)
 157 in the open waters of the north-west Pacific Ocean at a water depth of 3,244 m (Fig. 1). Samples
 158 from 2.85-2.55 Ma that have previously been analyzed for diatom $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{diatom}}$) and $\delta^{30}\text{Si}$
 159 ($\delta^{30}\text{Si}_{\text{diatom}}$) (Haug et al., 2005; Swann et al. 2006; Swann 2010, Bailey et al., 2011), using an age
 160 model derived from the astronomical calibration of high resolution GRAPE density and magnetic
 161 susceptibility measurements (Tiedemann and Haug, 1995), were re-analyzed for $\delta^{13}\text{C}_{\text{diatom}}$.
 162 Samples were previously cleaned and prepared for isotope analysis using standard
 163 methodologies for diatom isotope research involving chemical treatment with H_2O_2 , HCl and
 164 sieving with sample purity confirmed through light microscopy and SEM (see Swann et al., 2006
 165 for full details). All analyzed samples originated from the 75-150 μm fraction and are
 166 exceptionally well preserved with no signs of dissolution. This fraction is dominated by two taxa,
 167 *Coscinodiscus marginatus* (Ehrenb.) and *Coscinodiscus radiatus* (Ehrenb.), with *C. marginatus*
 168 dominating (c. > 90% relative biovolume abundance) until after the development of the halocline
 169 at 2.73 Ma when *C. radiatus* becomes dominant (see Supplementary Table 1; Fig. 2). Blooms of
 170 *C. marginatus* and *C. radiatus* occur through the year with elevated fluxes in autumn/early
 171 winter (Takahashi, 1986; Takahashi et al., 1996; Onodera et al., 2005). Consequently, the diatom
 172 isotope data obtained here are interpreted as primarily reflecting annually averaged conditions
 173 with a slight bias towards autumn/early winter months. All $\delta^{13}\text{C}_{\text{diatom}}$ analyses were completed
 174 using a Costech elemental analyzer linked to an Optima mass spectrometer via cold trapping at
 175 the NERC Isotope Geoscience Facility at the British Geological Survey (Hurrell et al., 2011).

176 A number of low-resolution foraminifera $\delta^{13}\text{C}$ records exist at ODP Site 882 over the
 177 iNHG (Maslin et al., 1996) and so can be used to monitor the $\delta^{13}\text{C}$ of the HCO_3^- substrate. For
 178 the purpose of this study only the planktonic *Globigerina bulloides* record is used due to its
 179 tendency to mainly calcify in the uppermost section of the water column at depths similar to the
 180 analyzed diatom taxa. For example, data from other available planktonic taxa, including
 181 *Neogloboquadrina pachyderma* (right + left coiling), are not comparable to $\delta^{13}\text{C}_{\text{diatom}}$ due to their
 182 scarcity in the sediment record and/or due to their potential to calcify at lower depths outside the
 183 photic zone. In an attempt to increase the resolution of the *G. bulloides* record, additional

184 samples were picked where possible and analyzed using an Isoprime Multiprep system attached
 185 to a GV Isoprime dual-inlet mass spectrometer as a tracer of $\delta^{13}\text{C}_{\text{DIC}}$. All $\delta^{13}\text{C}_{\text{diatom}}$ and $\delta^{13}\text{C}_{\text{foram}}$
 186 values are expressed on the V-PDB scale by reference to an internal laboratory standard
 187 calibrated against NBS-19 and NBS-22.

188 Other records from ODP Site 882 that are relevant to this study include estimates of sea
 189 surface salinity (SSS) ($\delta^{18}\text{O}_{\text{diatom}}$) and sea surface temperature (SST) (U_{37}^k) (Haug et al., 2005;
 190 Swann et al., 2006; Swann, 2010) which are required for calculating K_H in Equation 8. Values of
 191 $p\text{CO}_{2(\text{aq})}$ were reconstructed following Equations 1-8 using interpolated values of $\delta^{13}\text{C}_{\text{foram}}$, SST
 192 and SSS with $\delta^{13}\text{C}_{\text{foram}}$ measurements corrected for their offset from $\delta^{13}\text{C}_{\text{DIC}}$ following Spero and
 193 Lea (1996). Estimates of b were derived using existing opal concentrations data (Haug et al.,
 194 1999; Sigman et al., 2004) and calibrations for b published in Stoll et al. (2017) for centric taxa
 195 ($R^2 = 0.86$, $p < 0.01$). The uncertainty associated with b and $p\text{CO}_{2(\text{aq})}$ was calculated using Monte
 196 Carlo simulations (10,000 replicates) with the MonteCarlo package in R (Leschinski et al., 2017;
 197 R Core Team, 2017), assuming a normal distribution for proxy data uncertainty (SSS = 0.3 psu,
 198 SST = 1.2°C) in Equations 1-8.

199 3 Results

200 Analytical reproducibility (1σ) from replicate analysis of sample material was 0.3‰ and
 201 $<0.1\text{‰}$ for $\delta^{13}\text{C}_{\text{diatom}}$, and $\delta^{13}\text{C}_{\text{foram}}$ respectively. Over the analyzed interval through the
 202 Pliocene/early Quaternary, values of $\delta^{13}\text{C}_{\text{diatom}}$ range from -12.9‰ to -20.8‰ (Fig. 2,
 203 Supplementary Table 1). From 2.85-2.73 Ma values of $\delta^{13}\text{C}_{\text{diatom}}$ are near constant (mean =
 204 -14.1‰ , $1\sigma = 0.6\text{‰}$). Values of $\delta^{13}\text{C}_{\text{diatom}}$ then decrease for the remainder of the analyzed interval
 205 (mean = -18.0‰ , $1\sigma = 2.1\text{‰}$) in a shift that is concomitant with the marked decline in opal
 206 MAR at ODP Site 882. Through the post-iNHG interval significant variability is apparent in the
 207 $\delta^{13}\text{C}_{\text{diatom}}$ data with recurrent changes of up to 3-4‰ that do not coincide with further changes in
 208 opal MAR. Values of $\delta^{13}\text{C}_{\text{foram}}$ typically range from -0.46‰ to -0.95‰ with a shift to marginally
 209 higher values after the iNHG (Fig. 2). Despite efforts to increase the resolution of the $\delta^{13}\text{C}_{\text{foram}}$
 210 record, the number of data points declines after 2.73 Ma with sediments largely free of carbonate
 211 microfossils (Fig. 2).

212 Values of ϵ_p are at or below 5 until 2.73 Ma before increasing to >5 and a mean of 8 (Fig.
 213 3). Reconstructed $p\text{CO}_{2(\text{aq})}$ at ODP Site 882 typically range from c. 225-250 ppm with a peak
 214 value of 314 ppm at 2.81 Ma, a low of 192 ppm at 2.58 Ma and mean uncertainties of 39.5 ppm
 215 (1σ) (Fig. 3, Supplementary Table 1). From 2.85-2.73 Ma $p\text{CO}_{2(\text{aq})}$ displays a long-term decline
 216 from c. 280 ppm to c. 230 ppm ($\bar{x} = 247$ ppm; $1\sigma = 25$ ppm). Thereafter, from 2.71-2.55 Ma,
 217 $p\text{CO}_{2(\text{aq})}$ show a marked increase in variability with fluctuation of 20-60 ppm over the interval (\bar{x}
 218 = 225 ppm; $1\sigma = 28$ ppm).

219

220 4 Discussion

221 4.1 Changes in photic zone $p\text{CO}_{2(\text{aq})}$

222 High values of $\delta^{30}\text{Si}_{\text{diatom}}$ and opal MAR from 2.85-2.73 Ma indicate significant upwelling
 223 of nutrient-rich sub-surface waters which resulted in a productive water column marked by high
 224 rates of silicic acid [$\text{Si}(\text{OH})_4$] utilization (Haug et al., 1999; Sigman et al., 2004; Reynolds et al.,
 225 2008; Bailey et al., 2011; Swann et al., 2016) (Fig. 3). This situation contrasts with the post-2.73

Ma interval when the development of a halocline ceased significant upwelling and led to associated reductions in Si(OH)_4 utilization and siliceous productivity (Haug et al., 1999, 2005; Sigman et al., 2004; Swann et al., 2006; Reynolds et al., 2008; Swann et al., 2016) (Fig. 3). The presence of lower $p\text{CO}_{2(\text{aq})}$ after 2.73 Ma is consistent with these palaeoceanographic changes, namely a reduction in deeper CO_2 -rich waters reaching the photic zone under conditions of enhanced near-surface stratification. On this basis, the increased variability of $p\text{CO}_{2(\text{aq})}$ after 2.73 Ma may reflect changes in the strength of this stratification, an event which might impact the advection of carbon and nutrient rich deep water supply to the photic zone and so rates of Si(OH)_4 utilization. However, before and after the establishment of the halocline at 2.73 Ma, changes in $p\text{CO}_{2(\text{aq})}$ show no relationship to rates of Si(OH)_4 utilization, SSS or SST (Fig. 3).

4.2 Implications for ocean ventilation over the iNHG

To establish whether changes in subarctic Pacific $p\text{CO}_{2(\text{aq})}$ resulted in the region acting as a net sink or source of CO_2 , comparisons are needed to estimates of global $p\text{CO}_{2(\text{atm})}$. A number of modeled and proxy-based records have been published in recent years, but here we focus our comparisons on a recent multi-site $\delta^{13}\text{B}$ record which is the highest-resolution record to date and displays a decline in $p\text{CO}_{2(\text{atm})}$ of 40–90 ppm through the late Pliocene/early Pleistocene interval (Martinez-Boti et al., 2015). Calculation of $\Delta p\text{CO}_2$ (Eq. 9) between all $\delta^{13}\text{C}_{\text{diatom}}$ derived $p\text{CO}_{2(\text{aq})}$ at ODP Site 882 and interpolated $p\text{CO}_{2(\text{atm})}$ reveals considerable variation over the analyzed interval (Fig. 3). The mean age difference between the interpolated and original $p\text{CO}_{2(\text{atm})}$ data is 4.3 ka ($1\sigma = 3.7$ ka). With the exception of one sample at 2.81 Ma, values of $\Delta p\text{CO}_2$ are negative throughout the analyzed interval ($\bar{x} = -68$ ppm; $1\sigma = 43$ ppm). Whilst $\Delta p\text{CO}_2$ is lower after the development of the halocline at 2.73 Ma (pre-2.73 Ma: $\bar{x} = -61$ ppm; $1\sigma = 40$ ppm; post-2.73 Ma: $\bar{x} = -78$ ppm; $1\sigma = 47$ ppm), consistent with reduced upwelling of deep waters to the photic zone, this change is not significant ($p = 0.2$). The lack of a systematic shift in mean $\Delta p\text{CO}_2$ values after 2.73 Ma can be attributed to the large variations in both $p\text{CO}_{2(\text{aq})}$ and $\Delta p\text{CO}_2$ post-iNHG. More significantly, the results cast doubt on the notion that changes in the regional carbon dynamics in the subarctic Pacific Ocean played a key role in driving the iNHG. Although there is considerable variability in estimates of late Pliocene $p\text{CO}_{2(\text{atm})}$ both within and between individual studies (e.g., Pagani et al., 2010; Seki et al., 2010; Bartoli et al. 2011; van de Wal et al., 2011; Badger et al., 2013; Martínez-Boti et al. 2015; Willeit et al., 2015; Stap et al., 2016) in all cases reconstructed values of $p\text{CO}_{2(\text{atm})}$ remain above typical values of $p\text{CO}_{2(\text{aq})}$ at ODP Site 882. Values of $\Delta p\text{CO}_2$ at ODP Site 882 remains predominantly negative even when considering the Monte Carlo derived uncertainties for both $p\text{CO}_{2(\text{aq})}$ and $p\text{CO}_{2(\text{atm})}$ (Fig. 3).

Consistently low values of $\Delta p\text{CO}_2$ from 2.85–2.73 Ma suggest that the mixed water column that prevailed in the Pliocene prior to stratification did not release significant volumes of CO_2 to the atmosphere and so did not help maintain the warm Pliocene climate state. This interval in the ODP Site 882 record is marked by exceptional high opal concentrations of c. 60–75% (c. $2.2\text{--}3.2 \text{ g cm}^{-2} \text{ ka}^{-1}$) (Haug et al., 1999) and rates of Si(OH)_4 utilization (Swann et al., 2016) (Fig. 3). Consequently, although the mixed water column in this interval would have led to increased delivery of carbon rich waters to the surface, the negative values of $\Delta p\text{CO}_2$ suggest the associated flux of nutrients to the photic zone enabled a highly efficient biological pump that prevented carbon release from the ocean to the atmosphere (Fig. 3, 4a). We note, however, that this scenario is not supported by comparisons to the modern day where regions of strong upwelling and high diatom productivity/export remain net sources of CO_2 to the atmosphere (Takahashi et al., 2009; 2016). The uncertainties in using $\delta^{13}\text{C}_{\text{diatom}}$ to reconstruct $p\text{CO}_{2(\text{aq})}$ are discussed in Section 4.3. Whilst these indicate the issues in quantifying $p\text{CO}_{2(\text{aq})}$ and $\Delta p\text{CO}_2$ from

$\delta^{13}\text{C}_{\text{diatom}}$, thereby potentially explaining the anomalous negative values of $\Delta p\text{CO}_2$ at ODP Site 882, the underlying trends in $p\text{CO}_{2(\text{aq})}$ and $\Delta p\text{CO}_2$ can be used to understand regional late Pliocene/early Quaternary carbon dynamics in the subarctic Pacific. Although the development of the halocline at 2.73 Ma lowered $p\text{CO}_{2(\text{aq})}$ in line with reduced deep water upwelling, the absence of a bigger decline in $p\text{CO}_{2(\text{aq})}$ as well as $\Delta p\text{CO}_2$ is unexpected. After 2.73 Ma, opal concentration fall to c. 20-33% (c. $0.5\text{-}1.0\text{ g cm}^{-2}\text{ ka}^{-1}$) (Haug et al., 1999; Sigman et al., 2004) with corresponding declines in silicic acid utilization (Swann et al., 2016) (Fig. 3). We argue that a decline in $\text{Si}(\text{OH})_4$ utilization and the efficiency of biological export of carbon balanced out the reduced rate at which deep water carbon was advected to the photic zone, preventing a major decline in $p\text{CO}_{2(\text{aq})}$ or the net flux of CO_2 across the ocean-atmosphere interface ($\Delta p\text{CO}_2$) (Fig. 4b).

A number of models have indicated that a decline in $p\text{CO}_{2(\text{atm})}$ is critical for the development of large Northern Hemisphere ice-sheets (e.g., Lunt et al., 2008). With evidence presented here that carbon dynamics and $\Delta p\text{CO}_2$ did not significantly change in the subarctic North Pacific Ocean over the iNHG, the focus shifts to the Southern Ocean which plays a key role in regulating the c. 100 ppm variations in $p\text{CO}_{2(\text{atm})}$ over Pleistocene glacial-interglacial cycles (Sigman et al., 2010). Evidence for changes in Antarctic ice-sheet extent together with variations in Southern Ocean sea-ice and stratification through the Pliocene and oNHG (Hillenbrand and Cortese, 2006; Hodell and Venz-Curtis, 2006; Naish et al., 2009; Waddell et al., 2009; McKay et al., 2012) could have enhanced the ability of the Southern Ocean to act as a sink of atmospheric $p\text{CO}_{2(\text{atm})}$ through mechanisms that are analogous to those that occur in the Pleistocene (see Sigman et al., 2010). These processes could have been strengthened by increased aeolian iron deposition in the Southern Ocean over this interval, which would have increased the efficiency of the biological pump and the sequestration of carbon into the ocean interior (Martínez-García et al., 2011).

4.3 Uncertainties with $\delta^{13}\text{C}_{\text{diatom}}$

Despite measurements of $\delta^{13}\text{C}_{\text{diatom}}$ having been used in palaeoenvironmental reconstructions for over a decade to examine changes in photosynthetic carbon demand/productivity, its use to reconstruct $p\text{CO}_{2(\text{aq})}$ is relatively novel. Consequently, a discussion of the potential errors/limitations with $\delta^{13}\text{C}_{\text{diatom}}$ is appropriate to place the reconstructions of $p\text{CO}_{2(\text{aq})}$ at ODP Site 882 into a wider context.

4.3.1 Diatom carbon uptake

In contrast to foraminifera formed via the precipitation of HCO_3^- , diatoms uptake carbon from both HCO_3^- and $\text{CO}_{2(\text{aq})}$ through Carbon Concentrating Mechanisms (CCM) which enable the saturation of the enzyme RuBisCO that catalyses carbon fixation (Tortell et al., 1997). Such processes primarily involve either an active, direct, transportation of HCO_3^- and $\text{CO}_{2(\text{aq})}$ into the cell or an indirect HCO_3^- uptake in which an extracellular carbonic anhydrase (eCA) dehydrates HCO_3^- to CO_2 (Sültemeyer et al., 1993; Badger, 2003). In addition to these C_3 photosynthetic pathways, an indirect C_4 pathway has also been identified in which HCO_3^- is converted to malic or aspartic acid and then to CO_2 by decarboxylation (Reinfelder et al., 2000, 2004; Roberts et al., 2007).

Results from the Bering Sea, North Pacific, Equatorial Pacific and Southern Oceans show that significant, but variable, amounts of diatom carbon originates from HCO_3^- with the majority of this occurring via direct transportation (Tortell and Morel, 2002; Cassar et al., 2004; Martin

and Tortell, 2006, Tortell et al., 2006, 2008, 2010). Although $\text{HCO}_3^-:\text{CO}_{2(\text{aq})}$ uptake ratios may vary with large changes in pH (Trimborn et al., 2008) and inter-species variations in cell morphologies (Martin and Tortell, 2008), others have shown that this ratio does not change with $p\text{CO}_{2(\text{aq})}$, Fe availability, growth rates, primary productivity or frustule area:volume ratios (Cassar et al., 2004; Martin and Tortell, 2006, Tortell et al., 2006, 2008). The results presented here from ODP Site 882 do not account for any isotopic offset that may arise over the usage of HCO_3^- over CO_2 or the potential for active carbon uptake to alter ϵ_p (Burkhardt et al., 2001). For example, increases in $p\text{CO}_{2(\text{aq})}$ have been shown to downregulate CCM (Hennon et al., 2015), introducing a non-linear relationship between ϵ_p and $\delta^{13}\text{C}_{\text{diatom}}$ which impacts the ability to accurately reconstruct changes in $p\text{CO}_{2(\text{aq})}$ (Laws et al., 2002; Raven et al., 2011). Although these issues may impact the absolute values of reconstructed $p\text{CO}_{2(\text{aq})}$, we feel confident given the points made above that changes in $\text{HCO}_3^-:\text{CO}_2$ uptake ratios and transportation mechanism have not significantly altered over the analyzed interval or impacted the underlying trends in $p\text{CO}_{2(\text{aq})}$ and our assertion that the development of the halocline did not fundamentally alter regional carbon dynamics across the iNHG. For example, attempts to reconstruct $p\text{CO}_{2(\text{aq})}$ over the last 14 Ma using models that accounts for diffusive and active uptake of CO_2 by CCM results in different absolute values of $p\text{CO}_{2(\text{aq})}$ but similar temporal trends (Mejía et al., 2017).

4.3.2 Physiological factors

Physiological controls on the diffusion and fractionation of carbon into diatom, summarized by the term b (Equation 7), may change and alter $\delta^{13}\text{C}_{\text{diatom}}$ in response to different forms of RuBisCO, amino acids, growth rates, cell morphology and CCM (Laws et al., 1995, 2002; Rau et al., 1996, 1997, 2001; Rosenthal et al., 2000; Cassar et al., 2006; Scott et al., 2007), which in turn are potentially linked to evidence of a possible inter-species isotope vital effects in fossil measurements of $\delta^{13}\text{C}_{\text{diatom}}$ (Jacot Des Combes et al., 2008).

Within the context of this study the impact of isotope vital effects, other symbiont/physiological processes such as diatom cell size, geometry as well as the aforementioned $\text{HCO}_3^-:\text{CO}_2$ uptake process (Laws et al., 1995, 1997; Popp et al., 1998; Jacot des Combes et al., 2008; Martin and Tortell, 2008) can be partially circumvented by the use of a single size fraction of diatoms, dominated by only two taxa (Supplementary Table 1). This point is emphasized from 2.85-2.73 Ma when analyzed samples are dominated by *C. marginatus* (>90% relative abundance) and high nutrient concentrations would have created near-steady photic zone growth rates. Whilst declines in $\delta^{13}\text{C}_{\text{diatom}}$ and b as well as increases in ϵ_p coincide at 2.73 Ma with a change from *C. marginatus* to *C. radiatus* dominance in the analyzed samples, we attribute this change to the development of the regional halocline, with concordant changes in SST, SSS and opal concentrations, rather than an inter-species vital effect process (Fig. 2, 3). Whilst modern samples/culture experiments are needed to fully confirm the absence of an inter-species vital effect, we note that values of $\delta^{13}\text{C}_{\text{diatom}}$ both before ($R^2 = 0.01$) and after 2.73 Ma ($R^2 = -0.12$) are not related to the relative abundance of either *C. marginatus* or *C. radiatus* despite notable variation in the populations of both taxa in each interval (Supplementary Table 1). Finally, to fully account for physiological processes and reconstruct $p\text{CO}_2$ from $\delta^{13}\text{C}_{\text{diatom}}$, accurate estimates of b are required. Some previous studies have primarily based $p\text{CO}_2$ reconstructions from diatoms on growth rates (μ) (e.g., Rosenthal et al., 2000; Heuroux and Rickaby, 2015). Here we elect to directly constrain b based on the results of a Southern Ocean core-top study between the Polar Front and Southern Antarctic Circumpolar Current Front (Stoll et al., 2017). Despite calibrations being statistically significant, the standard error associated with this calibration results in a large uncertainty with the estimates of b used in this study ($1\sigma = 32.3$

362 ± 0.5). This, in turn, is the main source of the uncertainty derived in the Monte Carlo simulations
 363 for $p\text{CO}_{2(\text{aq})}$ (Fig. 3). It also remains unknown to what extent the Southern Ocean calibration of b
 364 can be directly applied elsewhere in the global ocean, to different taxa and/or through the
 365 geological record (Stoll et al., 2017), although these calibrations have been used on samples back
 366 to the Miocene (Mejía et al., 2017).

367 4.3.3 Underestimation of $p\text{CO}_{2(\text{aq})}$

368 In addition to the discussion above, we note that the reconstructed values of $p\text{CO}_{2(\text{aq})}$
 369 (173-288 ppm) are considerably lower than modern values of $p\text{CO}_{2(\text{aq})}$ (331-408 μatm) from 50-
 370 50.5°N and 167-168°E that have been collected over the past two decades in different seasons
 371 (Takahashi et al., 2016). The low values are also reflected in the reconstructed values of $\Delta p\text{CO}_2$
 372 over the analyzed interval (+15 ppm to -145 ppm; $\bar{x} = -68$ ppm; $1\sigma = 43$ ppm). In contrast,
 373 modern monthly $\Delta p\text{CO}_2$ from the region range from -50 μatm to +44 μatm (Takahashi et al.,
 374 2009) with mean annual preindustrial $\Delta p\text{CO}_2 + 3$ ppm ($p\text{CO}_{2(\text{aq})} = \text{c. } 280$ ppm; $p\text{CO}_{2(\text{atm})} = \text{c. } 277$)
 375 (JAMSTEC, 2013). Although comparing modern and palaeo estimates of $p\text{CO}_{2(\text{aq})}$ and $\Delta p\text{CO}_2$ is
 376 problematic given the storage of anthropogenic carbon and warming SST in the modern marine
 377 system, these lines of evidences suggest that our $\delta^{13}\text{C}_{\text{diatom}}$ reconstruction might underestimate the
 378 true values of $p\text{CO}_{2(\text{aq})}$ and $\Delta p\text{CO}_2$ at ODP Site 882 through the late Pliocene/early Quaternary.
 379 Whilst part of this underestimation may relate to differences in $p\text{CO}_{2(\text{aq})}$ seasonality before/after
 380 the development of the halocline, the impact of this is likely to be less than the Monte-Carlo
 381 inferred uncertainty of the $p\text{CO}_{2(\text{aq})}$ reconstruction (mean uncertainty = 39.5 ppm; see
 382 Supplementary Table 1). Given the limited work conducted to date on diatom b and its
 383 identification above as the main source of uncertainty in reconstructing $p\text{CO}_{2(\text{aq})}$ in this study, we
 384 suggest that further calibrations of this parameter are needed outside of the Southern Ocean and
 385 involving a greater range of taxa. Notwithstanding this issue, based on current knowledge we
 386 remain confident in the overall trend and magnitude of change in our reconstructed record of
 387 $p\text{CO}_{2(\text{aq})}$ and $\Delta p\text{CO}_2$. As such, we reiterate our main finding that the development of the halocline
 388 in the subarctic north-west Pacific Ocean at 2.73 Ma did not lead to a major change in regional
 389 marine-atmospheric fluxes of CO_2 and that therefore carbon dynamics in the region did not play
 390 a major role in aiding the iNHG.

391 5 Conclusions

392 Understanding the potential sources and sinks of atmospheric CO_2 that helped regulate
 393 the global climate through the late Pliocene is of critical importance given the interval's potential
 394 to act as an analogue for a warmer climate state in the 21st Century and beyond. New results
 395 based on $\delta^{13}\text{C}_{\text{diatom}}$ from ODP Site 882 in the north-west subarctic Pacific Ocean show that
 396 regional ocean-atmospheric exchanges of CO_2 did not fundamental alter over the iNHG. This
 397 occurred despite a reduction in the upwelling of high- $p\text{CO}_{2(\text{aq})}$ deep waters at 2.73 Ma that were
 398 balanced by a corresponding reduction in carbon export by a less efficient biological pump.
 399 Whilst uncertainties exist in using $\delta^{13}\text{C}_{\text{diatom}}$ to reconstruct $p\text{CO}_{2(\text{aq})}$ and $\Delta p\text{CO}_2$, highlighting the
 400 need for more modern calibrations in particular for the term b , the results suggest that any
 401 decline in $p\text{CO}_{2(\text{atm})}$ through the late Pliocene and early Quaternary was not driven by changes in
 402 the north-west subarctic Pacific Ocean.

403 Acknowledgements, Samples, and Data

Supporting data ($\delta^{13}\text{C}_{\text{diatom}}$ and $p\text{CO}_{2(\text{aq})}$ data together with the diatom species composition of analyzed samples from ODP Site 882 between 2.85 Ma and 2.55 Ma) are included as a spreadsheet in the SI. This work was supported by the Natural Environment Research Council and a NERC postdoctoral fellowship award to GEAS (grant numbers NE/F012969/1, NE/F012969/2). We thank the staff at the IODP Gulf Coast Core Repository for providing samples and sampling cores from ODP Site 882 in addition to Carol Arrowsmith for assistance with the $\delta^{13}\text{C}_{\text{diatom}}$ analyses and Hilary Sloane for analyzing the additional planktonic $\delta^{13}\text{C}_{\text{foram}}$ samples. Finally, thanks are owed to the two anonymous reviewers and the editor (Stephen Barker) who's comments significantly improved the manuscript.

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Figure 1. Location of ODP Site 882 (50°22'N, 167°36'E) in the north-west subarctic Pacific Ocean. Colours indicate annual modern gridded surface water $p\text{CO}_{2(\text{aq})}$ (Takahashi et al., 2016). Map created using Ocean Data View (<https://odv.awi.de>).

Figure 2. Late Pliocene/early Quaternary palaeoceanographic records from ODP Site 882. Changes in $\delta^{18}\text{O}_{\text{diatom}}$ derived SSS (Swann et al., 2006; 2010), U^k_{37} derived SST (Haug et al., 2005), $\delta^{13}\text{C}_{\text{foram}}$ (*G. bulloides*) (Maslin et al., 1996, 1998; this study) and $\delta^{13}\text{C}_{\text{diatom}}$, used to reconstruct $p\text{CO}_{2(\text{aq})}$ (Equation 1-9), are compared to the relative diatom species biovolume in samples analyzed for $\delta^{13}\text{C}_{\text{diatom}}$. Orange dashed line denotes transition from unstratified to stratified water column at 2.73 Ma with gray (white) shading reflecting glacial (interglacial) intervals.

Figure 3. Temporal changes in carbon dynamics at ODP Site 882. Values of $\delta^{13}\text{C}_{\text{diatom}}$, ϵ_p , b and $p\text{CO}_{2(\text{aq})}$ are compared to $p\text{CO}_{2(\text{atm})}$ (Martinez-Boti et al., 2015) and used to calculate $\Delta p\text{CO}_2$. Shaded polygons for b , $p\text{CO}_{2(\text{aq})}$, $p\text{CO}_{2(\text{atm})}$ and $\Delta p\text{CO}_2$ reflect the 1 σ uncertainty derived from Monte-Carlo simulations. Changes in opal concentrations (Haug et al., 1999; Sigman et al., 2004) and rates of Si(OH)₄ utilization (Swann et al., 2016) provide information on the biological pump and the export of carbon into the ocean interior. Orange dashed line denotes transition from unstratified to stratified water column at 2.73 Ma with gray (white) shading reflecting glacial (interglacial) intervals.

Figure 4. Conceptual model of the palaeoceanographic changes in the north-west subarctic Pacific Ocean. A) From 2.85-2.73 Ma an unstratified water column leads to unimpeded upwelling of deep water. The transportation of nutrients and carbon rich waters to the photic

742 zone is compensated by high levels of siliceous productivity and Si(OH)_4 utilization creating a
743 highly efficient biological pump that minimizes CO_2 leakage to the atmosphere. B) Following the
744 development of the halocline, deep waters are limited from reaching the photic zone. The
745 corresponding decline in both the strength and efficiency of the biological pump, however,
746 results in the net ocean-atmospheric flux of CO_2 remaining similar to conditions prior to 2.73 Ma
747 with only minor decreases in $p\text{CO}_{2(\text{aq})}$ and $\Delta p\text{CO}_2$.

Figure 1

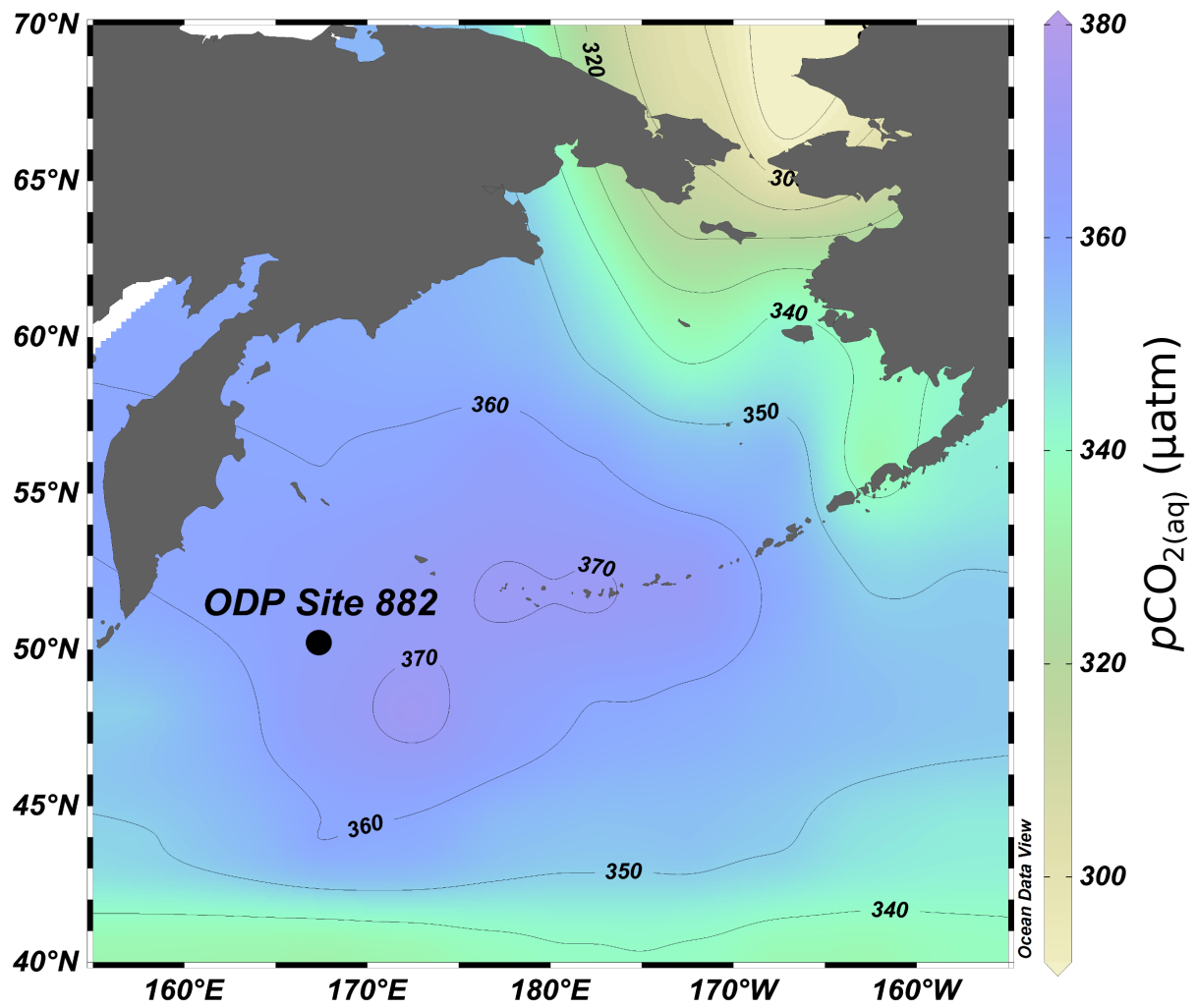


Figure 2

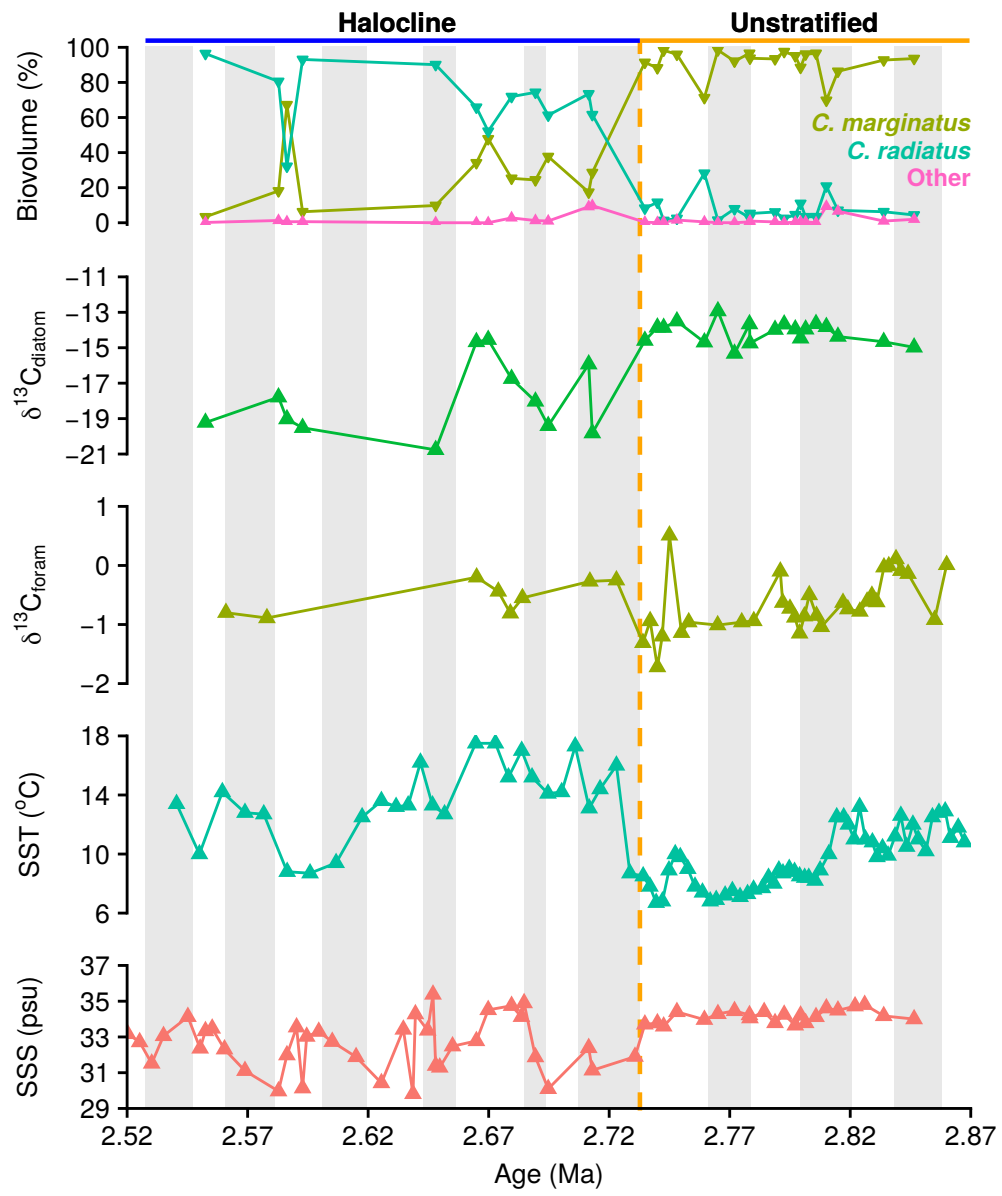


Figure 3

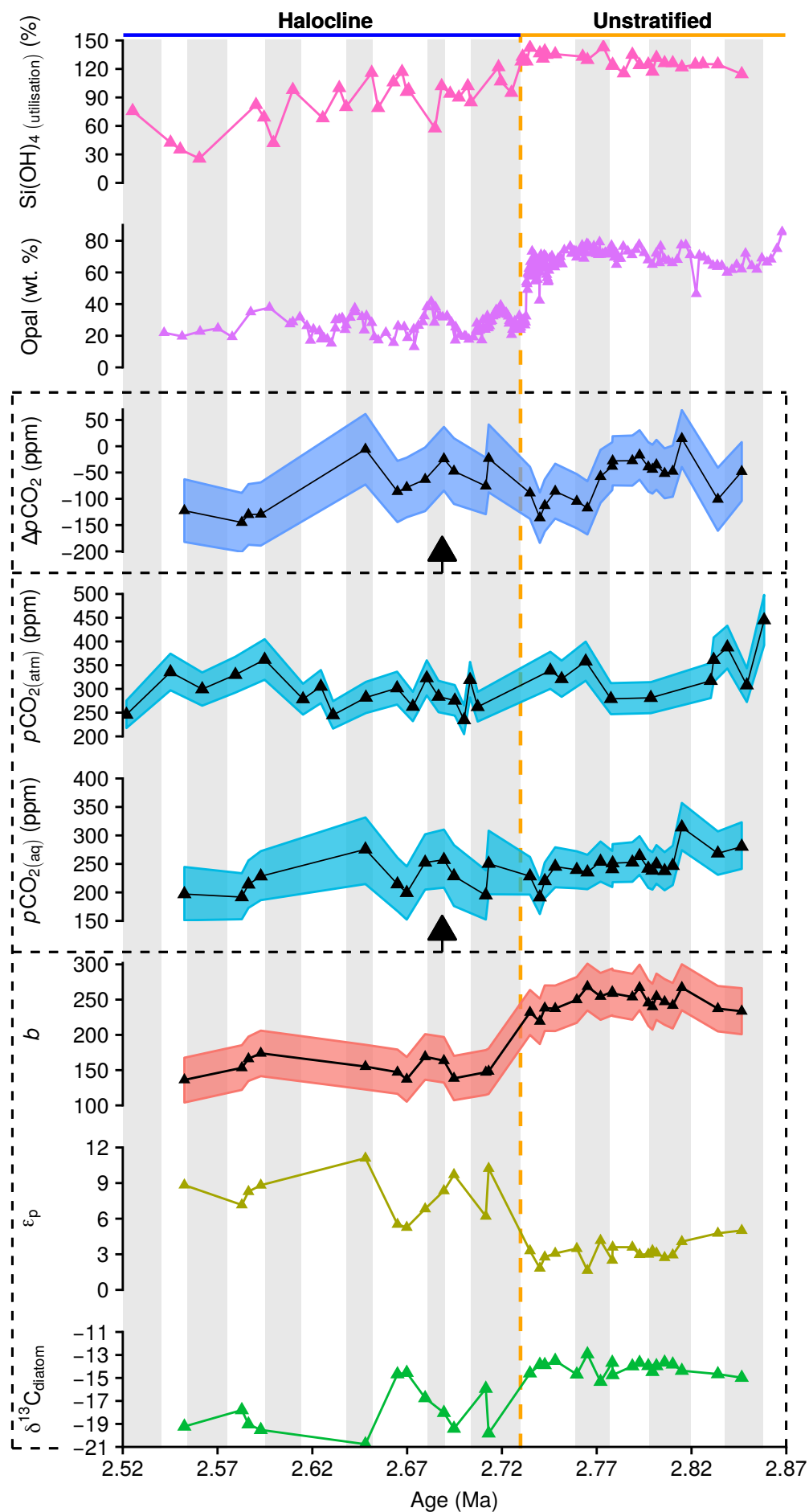


Figure 4

